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Relationships between Electronic Spectroscopy and Electrochemistry.

A Probe of Reorganisation Energies

BY

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The electronic spectra and electrochemical potentials of the species $[Ru(bipy)_x(NN)_{3-x}]^{2+}$ (bipy = 2,2'-bipyridine, NN = unsaturated diimine, x = 1,2] are correlated via fundamental relationships involving reorganisation and solvation energies. It is argued that the presence of two distinct $Ru \rightarrow$ ligand charge transfer transitions allows comparison of the reorganisation energies therefore. Originator supplied keywords include:-

Relationships between Electronic Spectroscopy and Electrochemistry. A Probe of Reorganisation Energies

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Abstract

The electronic spectra and electrochemical potentials of the species $[Ru(bipy)_x(NN)_{3-x}]^{2+}$ (bipy = 2,2'-bipyridine, NN = unsaturated diimine, $x = 1,2$] are correlated via fundamental relationships involving reorganisation and solvation energies. It is argued that the presence of two distinct Ru$\longrightarrow$ligand charge transfer transitions allows comparison of the reorganisation energies therefore.

We have recently been concerned [1-3], as have others [4-9], with relationships between optical transition energies and electrochemical potentials. Such a study may reveal details concerning the various solvation energies, and the inner and outer reorganisation energies involved in the two measurements. So far interest has centred on a single charge transfer transition between states involving levels ψ_g and ψ_e and the electrochemical potentials for oxidation of the former and reduction of the latter.

The relationship is complicated by the inclusion of solvation energies of the oxidised and reduced molecule, and of the Franck-Condon (non-equilibrium) excited state, but it seems that it might be simplified if two (or more) charge transfer (CT) transitions in one molecule are considered.

We choose to study complexes of the type $[Ru(II)(bipy)_x(NN)_{3-x}]^{2+}$ (bipy = 2,2'-bipyridine, x = 1,2, and (NN) = unsaturated diimine) for which both electrochemical and optical data are available in the literature. Further we specify that the diimine be reduced at a potential at least 0.2V more positive than bipyridine. Under such conditions it is possible to identify separate electrochemical potentials for the reduction of each ligand, and separate charge transfer transitions to each ligand, $Ru(II)(d) \longrightarrow \pi^*(NN)$ and $Ru(II)(d) \longrightarrow \pi^*(bipy)$, the former at lower energy [7,8,10-13]. The π^* acceptor orbitals on each ligand are considered to be "spatially isolated" i.e. the excited state is localised on one ligand [14-18].

The first reduction potential of such a system, say $E_r(1)$ (the number refers to the equation number), corresponds with the couple:-

$$[Ru(II)(bipy)_2(NN)]^{2+} + e^- \longrightarrow [Ru(II)(bipy)_2(NN)^-]^+$$

(1)
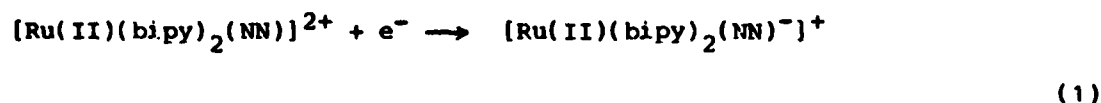
and the second reduction potential, $E_r(2)$, corresponds with:-

$$[Ru(II)(bipy)_2(NN)^-]^+ + e^- \longrightarrow [Ru(II)(bipy)_2^-(NN)^-]$$

(2)
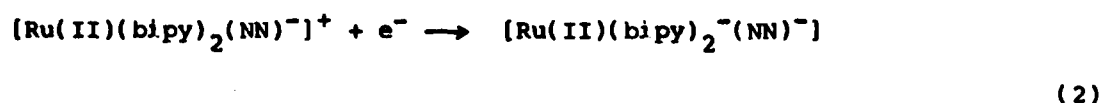
where it is important to note that the measured potential involves addition of an electron to bound bipyridine in a molecule in which an electron has already been added to diimine (NN). These couples involve addition of an electron to orbitals on bipy or (NN) which are directly involved in the CT transition. Of relevance to the optical transition is the couple with potential $E_r(3)$:-

$$[Ru(II)(bipy)_2(NN)]^{2+} + e^- \longrightarrow [Ru(II)(bipy)_2^-(NN)]^+$$

(3)
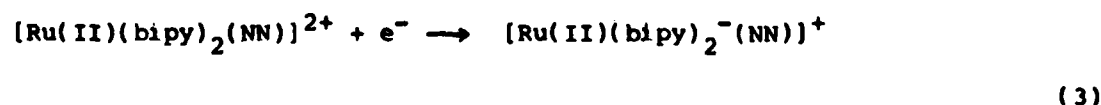
which cannot be directly observed electrochemically. Also necessary is

the potential $E_r(4)$ for the process:-

$$[Ru(III)(bipy)_2(NN)]^{3+} + e^- \longrightarrow [Ru(II)(bipy)_2(NN)]^{2+}$$

(4)
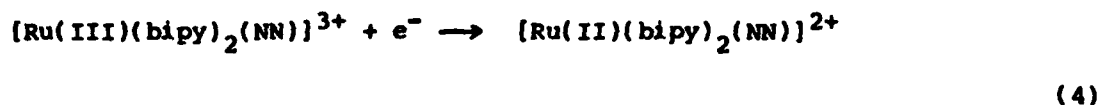
which is a measure of the potential of the d electron on Ru(II) involved in excitation in both CT transitions [19].

It is also useful to define some redox potential differences involving these orbitals, namely:-

$$\Delta E1(redox) = E_r(4) - E_r(1)$$

$$\Delta E2(redox) = E_r(4) - E_r(2)$$

$$\Delta E3(redox) = E_r(4) - E_r(3)$$

(5)

where the first two are obtainable directly from the voltammograms. Then following [1], the relationship between the optical transition, E_{op}, and the redox energy may be written as follows, the square bracketed term being solvent independent:-

$$E_{op} = [X_i + \Delta\Delta G_s + \Delta Ei(redox) + Q] + X_o + \Delta(sol) \quad (Ei = E1 \text{ or } E3)$$

(6)

where X_i and X_o are the inner(vibrational) and outer(solvation) reorganisation energies, Q is the energy required for the gas phase process $(ML^{3+})_g + (ML^+)_g \longrightarrow (ML^{2+})_g + (ML^{2+*})_g$, $\Delta\Delta G_s = 2\Delta G_s(2+) - \Delta G_s(3+) - \Delta G_s(1+)$, and $\Delta(sol) = \Delta G_s(2+*) - \Delta G_s(2+)$; the various ΔG_s terms are the solvation free energies for parent species, ML^{2+}, its oxidised and reduced species, and its equilibrated excited charge transfer state, ML^{2+*}. Terms involving the excited state, and those involving ML^+, will generally differ for the two CT transitions concerned. Possible configurational interaction between the CT state and another nearby state of the same symmetry is not

accounted for in this expression.

Recently Ohsawa, Hanck and DeArmond have also addressed the relationships between optical CT spectra and electrochemical data [7]. Their somewhat less extensive analysis concerns the absorption and emission spectra of a similar series of complexes. Their approach is fundamentally similar to this.

Rearrangement of eqn.(6) and insertion of the appropriate ΔE_i(redox) term leads to:-

$$E_{op}(NN) - \Delta E1(redox) = \{ \chi_i + \Delta\Delta G_s + Q + \chi_o + \Delta(sol) \}_{NN}$$

$$E_{op}(bipy) - \Delta E3(redox) = \{ \chi_i + \Delta\Delta G_s + Q + \chi_o + \Delta(sol) \}_{bipy}$$

(7)

Use of Eqn.(7) with the second MLCT transition, to bipy, involves $\Delta E3$(redox) which is not measurable directly but can be estimated within certain error limits. Thus $\Delta E2$(redox) is directly observable and it must be true that $|\Delta E2(redox)| > |\Delta E3(redox)|$. Considering the $[Ru(bipy)_3]^{2+}$ ion, the second reduction potential is 0.18V more negative than the first [10], a consequence of a change in charge, differential solvation, spin-repulsion and ligand-ligand interactions [20]. The first three of these effects should be comparable, for these mixed ligand systems, to those for the $[Ru(bipy)_3]^{2+}$ ion, while the last is accounted for within the reduction potential observed. We argue then that couple (2), $E_r(2)$, is also displaced on average 0.18V from couple (3), $E_r(3)$, and write for the bis(bipy) series:-

$$\Delta E3(redox) = \Delta E2(redox) - 0.18 \text{ (in V)}$$

(8)

The data in Table 1 may be used directly in solving eqn.(7) for the

$Ru \longrightarrow \pi^*(NN)$ transition, and eqn.(7) may be evaluated for the MLCT transition to bipy via use of eqn.(8). Columns 2 and 3 of Table 2 contain such data relating to the two charge transfer transitions and show that the sum of terms on the right of eqn.(7) is almost invariably positive and quite small.

This sum is not expected to vary greatly for the $Ru \longrightarrow \pi^*(bipy)$ transition in a series of complexes; excluding complexes of (11) and (14), it lies between 0.19 and 0.34eV. The two excluded complexes are anomalous, having smaller or negative values for the rhs of eqn.(7). This is probably a consequence of the $Ru \longrightarrow \pi^*(bipy)$ transition being a shoulder in both cases so that its peak position is not accurately reported. Data for the $Ru \longrightarrow \pi^*(NN)$ transitions in these two species are consistent with the other data.

These arguments may be extended to species of the type $[Ru(bipy)(NN)_2]^{2+}$. Diimines (NN) are chosen in which the first two reduction potentials refer to sequential reduction of each diimine, and the third refers to reduction of bipyridine. Eqn.(7) may be solved directly for the lowest charge transfer transition to the diimine ligand (Tables 1,2). The third reduction potential, $E_r(9)$, of the species, namely:-

$$[Ru(II)(bipy)(NN)_2{}^{2-}] + e^- \longrightarrow [Ru(II)(bipy)^-(NN)_2{}^{2-}]^-$$

$$(9)$$
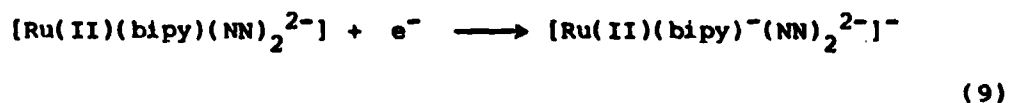
can be measured, while to solve eqn.(7) for the $Ru \longrightarrow \pi^*(bipy)$ CT transition in these mono(bipy) series, $E_r(10)$ is required:-

$$[Ru(II)(bipy)(NN)_2]^{2+} + e^- \longrightarrow [Ru(II)(bipy)^-(NN)_2]^+$$

$$(10)$$
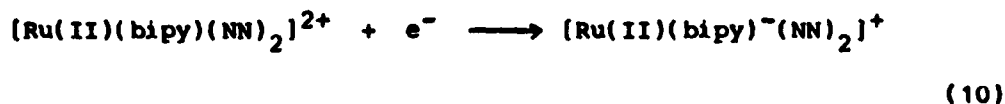
$\Delta E9(redox)$ and $\Delta E10(redox)$ are defined as the (positive) differences

between each of these last two reduction potentials and the potential $E[(Ru(III)(bipy)(NN)_2)^{3+}/(Ru(II)(bipy)(NN)_2)^{2+}]$. Using an argument similar to that above, and noting that the third reduction potential of $[Ru(bipy)_3]^{2+}$ is 0.43V more negative than the first, it is estimated that:-

$$\Delta E10(redox) = \Delta E9(redox) - 0.43 \text{ (in V)}$$

(11)

Evaluation of eqn.(7) for this mono(bipy) series also reveals small positive values of the rhs of eqn.(7) (Table 2). There are insufficient data to test the evaluation of eqn.(7) thoroughly; however, various individual terms can be evaluated separately and will be sought. Note that, as shown in Fig.1, most of the data (both CT bands, both series of complexes) fall on essentially the same line though with obvious scatter. Excluding the three data points for the $Ru \longrightarrow \pi^*(bipy)$ transition in the mono(bipy) series, and the two data points for complexes of (11) and (14) mentioned above, the equation of this line (26 data points) is:-

$$E_{op}(CT) = 1.27\Delta Ei(redox) - 0.45 \qquad \text{(in eV)}$$

(12)

with a regression coefficient of 0.97. The three data points not included would lie on the line if the correction in eqn.(11) were increased slightly. Ghosh and Chakravorty report a similar relationship but fix the slope to unity [21]. There seems no justification for so doing since some of the terms in eqn.(7) may also vary as $\Delta Ei(redox)$ varies. The single line dependence, if real, would mitigate against obtaining useful information since it would imply that the collection of parameters on the rhs of eqn.(7) was independent of the diimine

ligand. Rather, the apparent agreement reflects the relatively small,
but not zero, contribution of these terms.

Alternatively, following the development in [2], but including the
reorganisation energies, the optical transition energy may be written
(e.g. for the $Ru \longrightarrow \pi^*$(bipy) transition):-

$$E_{op}(bipy) = E[(Ru(III)(bipy)_2^-(NN))^{2+}/(Ru(II)(bipy)_2^-(NN))^+]$$

$$- E[(Ru(II)(bipy)_2(NN))^{2+}/(Ru(II)(bipy)_2^-(NN))^+] + X_i + X_o$$

$$(13)$$

The Ru(III) product in the first potential of the above equation is in
the singlet state. The difference between the two CT transitions may
now be written, following eqn.(13), in terms of two redox potential
differences:-

$$E_{op}(bipy) - E_{op}(NN) = \Delta E'[Ru(III)/Ru(II)] - [E_r(3) - E_r(1)] + \Delta X_i + \Delta X_o$$

$$= \Delta E'[Ru(III)/Ru(II)] + E_r(1-3) + \Delta X_i + \Delta X_o$$

$$(14)$$

where $\Delta E'[Ru(III)/Ru(II)]$ is the difference in the Ru(III)/Ru(II) redox
couples when the ruthenium atom is bound to reduced bipy and to reduced
(NN), and $\Delta E_r(1-3) = E_r(1) - E_r(3)$.
The parameters ΔX_i and ΔX_o are the differences respectively of χ_i and
X_o for the CT transitions to bipy and (NN).

$\Delta E_r(1-3)$ for the bis(bipy) series is obtainable via the above
development as:-

$$\Delta E_r(1-3) = E_r(1) - E_r(2) - 0.18 \text{ (in V)}$$

$$(15)$$

with a similar equation involving 0.43V for the mono(bipy) series.
$\Delta E'[Ru(III)/Ru(II)]$ is not directly measurable but is likely to be very

small, and can almost certainly be neglected. This assumption does not

take into account effects of configurational interaction, which,

however, are implicitly included in (13) and (14). Note that

comparison of eqns.(7) and (14) shows that, with this assumption,

$\Delta E'[Ru(III)/Ru(II)] = \Delta(\Delta\Delta G_s) + \Delta Q + \Delta(\Delta(sol)) = 0$, not unreasonable

since these various differences refer to differences relating to

reduced bipyridine or (NN) in the same molecule. Hence:-

$$E_{op}(bipy) - E_{op}(NN) = E_r(1) - E_r(2) - 0.18 + \Delta X_i + \Delta X_o$$

$$\text{(all data in V)} \quad \text{[bis(bipy) series]} \qquad (16)$$

$$E_{op}(bipy) - E_{op}(NN) = E_r(1) - E_r(2) - 0.43 + \Delta X_i + \Delta X_o$$

$$\text{(all data in V)} \quad \text{[mono(bipy) series]} \qquad (17)$$

These equations may be solved to yield values of the relative total

reorganisation energy, $\Delta X_i + \Delta X_o$ [(bipy) - (NN)], as shown in Table 2.

The sum may be positive or negative but is quite small, and of the same

order of magnitude as the experimental errors in E_{op} and ΔE_i(redox).

However the spread in values exceeds these experimental errors.

The $Ru \longrightarrow \pi^*$(bipy) CT transitions in [Ru(bipy)$_3$]$^{2+}$ [15] and in many

Ru(bipy)$_2$X$_2$ are not strongly solvatochromic [22-24]. Preliminary

studies of the solvatochromism of [Ru(bipy)(Bpz)$_2$]$^{2+}$ show only small

changes for both relevant CT transitions, the transition to bipy being

less solvent dependent. Following the procedure in [1] (solving

eqns.(7) and (8) therein), and assuming the validity of the dielectric

continuum model, approximate values of 1400 cm^{-1} and 1700 cm^{-1} are

calculated for X_o for $Ru \longrightarrow \pi^*$(Bpz) and $Ru \longrightarrow \pi^*$(bipy) respectively, with

rather greater uncertainty in the latter case. A similar value

(1100 cm^{-1}) can be calculated for the $Os \longrightarrow \pi^*$(bipy) transition in

[Os(bipy)$_2$(CH$_3$CN)$_2$]$^{2+}$, using data in [15].

It is probable that X_o lies around 1400$\pm$300 cm^{-1} (=0.17$\pm$0.04eV).

The magnitude and variation in χ_o are therefore comparable to the magnitude and variation of the sum of terms of the rhs of Eqn.(7). Thus it is difficult to distinguish contributions from χ_i and χ_o, when the relative total reorganisation energy,$\Delta\chi$, is considered.

If it is assumed that the total reorganisation energy, χ, for the Ru$\longrightarrow\pi^*$(bipy) transition is roughly constant, the variation in the sum will reflect the variation in χ for Ru$\longrightarrow\pi^*$(NN). Thus within the series of ligands in Table 1, and using the nomenclature in [10] (also see footnotes to Table 1), χ (NN) decreases in the sequence (bis(bipy) series):-

$$(7) = (8) > bipy > Bpz > BX > BL > Bpyrm > (9) = (10) = (12) = (13)$$

$$(18)$$

The above assumption is almost certainly justified for the series of complexes in [10], which have very similar structures, but is perhaps questionable for the other species in expression (18). It is significant that for the series in [10], ligands with the same number of methylene groups bridging the 3,3' position [10] have equal values of $\Delta\chi$. The reorganisation energies of the Ru$\longrightarrow\pi^*$(NN) transitions in the complexes of (7) and (8) are certainly greater than for those of (9), (10), (12) and (13). Molecular models show that (7) and (8) contain very strained 5-membered rings, whereas the other four contain 6- or 7-membered rings in which there is little or no strain. Since it is the bridging group linking the 3,3' position, and not the substituent (Me or Ph) at the 4,4' position, which appears to determine the variation in $\Delta\chi$, it is probable that the variation in total χ is reflecting a variation in χ_i rather than χ_o, i.e there is a relationship between ground state strain and χ_i.

Future studies will test these ideas with a larger data base and

with a variable temperature study of both optical spectra and electrochemistry.

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19. This may not always be strictly accurate since it will depend upon the
    symmetries and relative energies of the d orbitals within the t_{2g} set.
    This problem is addressed elsewhere [22]. It is not an unreasonable
    assumption for the purpose of this discussion.

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Table 1
Optical Charge Transfer Energies and Electrochemical Potentials for $[Ru(bipy)_2(NN)]^{2+}$ and $[Ru(bipy)(NN)_2]^{2+}$ Systems

NN[b]	Electrochemical Potentials (V)			Ref. Elect.[a]	Optical Charge Transfer Energies (cm^{-1})		Ref
	$(Ru^{3}+/Ru^{2+})$	(NN/NN^-)	$(bipy/bipy^-)$		$Ru \rightarrow (NN)$	$Ru \rightarrow (bipy)$	
$[Ru(bipy)_2(NN)]^{2+}$							
(7	1.260	−1.030	−1.485	nhe	20,150	22,250	10
(8)	1.295	−0.895	−1.440	nhe	19,550	22,400	10
(9)	1.310	−0.910	−1.385	nhe	18,950	22,750	10
(10)	1.255	−1.000	−1.410	nhe	18,950	22,300	10
(11)	1.300	−0.905	−1.365	nhe	18,800	20,150sh	10
(12)	1.240	−1.080	−1.435	nhe	19,950	22,850	10
(13)	1.290	−0.990	−1.400	nhe	19,400	22,750	10
(14)	1.330	−0.905	−1.370	nhe	19,000	20,250sh	10
Bpz	1.49	−0.91	−1.45	ssce	21,150	24,150	13
Bpyrm	1.40	−1.02	−1.45	ssce	20,850sh	23,700	13
BL	1.41	−0.72	−1.41	ssce	19,050	23,800sh	11
BX	1.41	−0.78	−1.41	ssce	19,400	23,400sh	12
$[Ru(bipy)(NN)_2]^{2+}$							
(10)	1.255	−0.920	−1.665	nhe	17,900	20,450	10
		−1.135					
(14)	1.395	−0.820	−1.610	nhe	18,300	20,800	10
		−1.050					
Bpz	1.72	−0.79	−1.58	ssce	21,600	24,100	13
		−1.02					
Bpyrm	1.55	−0.95	(ob)	ssce	21,750sh	23,800	13
		−1.13					

a) nhe = normal hydrogen electrode, ssce = saturated sodium chloride electrode. All data collected in acetonitrile. Since we consider here

only differences in potential, the reference electrode potential cancels out. b) Bold numbers refer to ligands in Ref.[10] which also includes diagrams.

(7) = 3,3'-methylene-4,4'-dimethyl-2,2'-biquinolyl, (8) = 3,3'-methylene-4,4'-diphenyl-2,2'-biquinolyl, (9) = 3,3'-dimethylene-2,2'-biquinolyl, (10) = 3,3'-dimethylene-4,4'-dimethyl-2,2'-biquinolyl, (11) = 3,3'-dimethylene-4,4'-diphenyl-2,2'-biquinolyl, (12) = 3,3'-trimethylene-4,4'-dimethyl-2,2'-biquinolyl, (13) = 3,3'-trimethylene-4,4'-diphenyl-2,2'-biquinolyl, (14) = 2,2'-biquinolyl, BL = 2,2',3,3'-tetra-2-pyridyl-6,6'-biquinoxaline, BX = 2,3-di-2-pyridylquinoxaline, Bpyrm = 2,2'-bipyrimidine, Bpz = 2,2'-bipyrazine.

ob = osbcured. sh = shoulder.

Table 2
Solutions to Eqn.(7) and Evaluation of $\Delta X_i + \Delta X_o$ for $[Ru(bipy)_2(NN)]^{2+}$ and $[Ru(bipy)(NN)_2]^{2+}$ Systems[a]

	Solns. to rhs of eqn.(7)		Eqn.(13)
	$Ru \longrightarrow \pi^*(NN)$	$Ru \longrightarrow \pi^*(bipy)$	$\Delta X_i + \Delta X_o$ [b]
$[Ru(bipy)_2(NN)]^{2+}$			
(7)	0.21	0.19	-0.02
(8)	0.23	0.22	-0.01
(9)	0.13	0.31	0.18
(10)	0.09	0.28	0.19
(11)	0.13	0.01[c]	-0.12
(12)	0.15	0.34	0.19
(13)	0.13	0.31	0.18
(14)	0.12	-0.01[c]	-0.13
Bpz	0.22	0.23	0.01
Bpyrm	0.17	0.27	0.10
BL	0.23	0.31	0.08
BX	0.22	0.26	0.04
$[Ru(bipy)(NN)_2]^{2+}$			
(10)	0.04	0.05[d]	0.01
(14)	0.05	0[d]	-0.05
Bpz	0.17	0.12[d]	-0.05
Bpyrm	0.20	-	-

a) All data in volts. See Table 1 for raw optical and electrochemical data and nature of the ligands. b) A negative number implies a reorganisation energy for $Ru \longrightarrow \pi^*(NN)$ greater than for $Ru \longrightarrow \pi^*(bipy)$. c) Anomalous - see text. d) These values are underestimated if, as suspected, the 0.43V correction in eqn.(11) is underestimated. In both cases c) and d), the corresponding numbers in column 4 should probably be more positive.
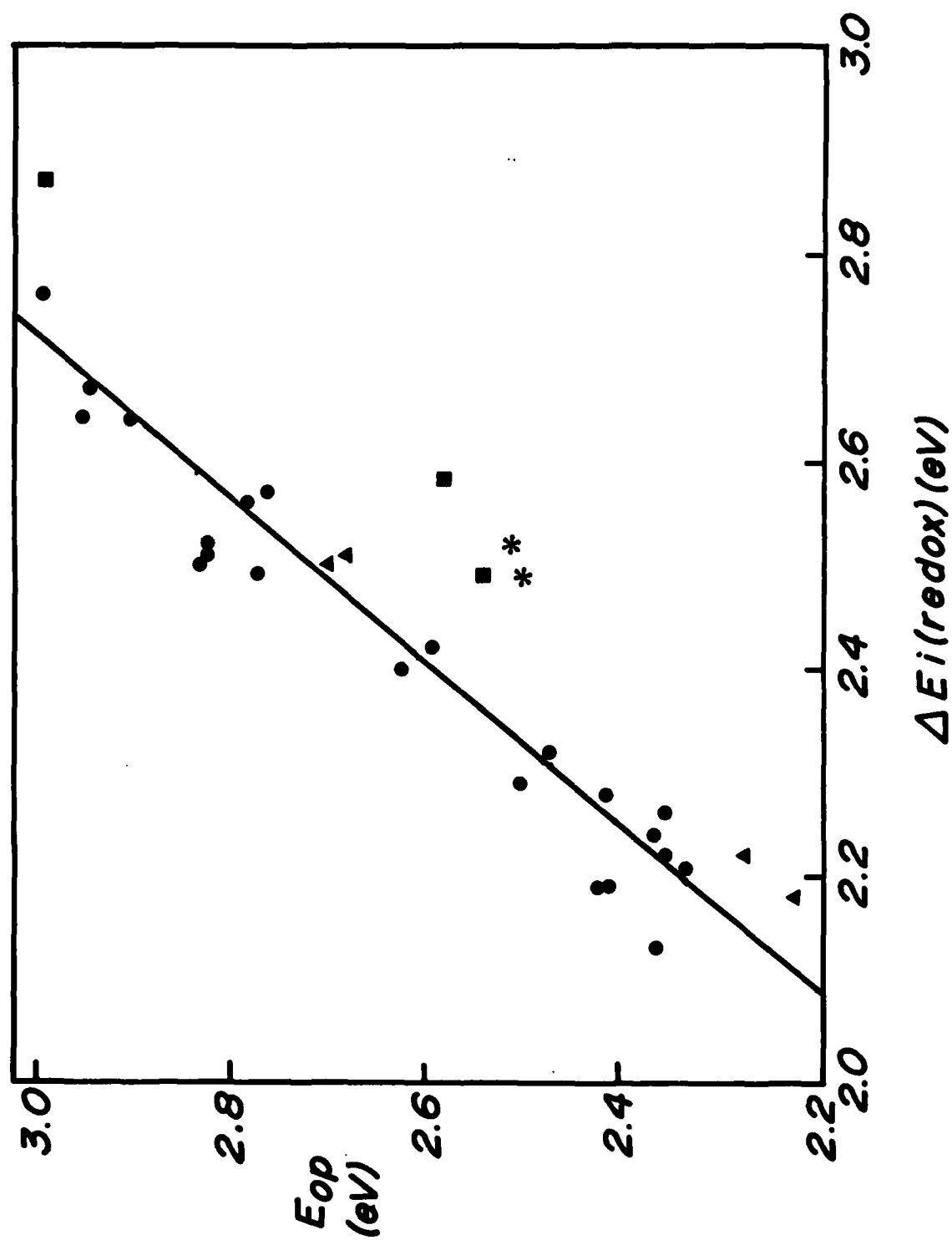
Figure Legend

A plot of the Ru$\longrightarrow\pi^*$(NN) and Ru$\longrightarrow\pi^*$(bipy) transition energies against the appropriate value of ΔEi(redox) according to eqns. (5), (8) and (11). The data are as in Table 1 but converted to eV (1eV = 8065 cm^{-1}). $[Ru(bipy)_2(NN)]^{2+}$: ● Ru$\longrightarrow\pi^*$(NN) and Ru$\longrightarrow\pi^*$(bipy) excluding (11) and (14); ＊ Ru$\longrightarrow\pi^*$(bipy) for (11) and (14). $[Ru(bipy)(NN)_2]^{2+}$: ▲ Ru$\longrightarrow\pi^*$(NN); ■ Ru$\longrightarrow\pi^*$(bipy). The least squares line (eqn.12) does not include (11) and (14).

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